

Landfill Gas Conversion to a Contaminant-Free Methane-Carbon Dioxide Reformer Feedstock for Methanol Synthesis

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Introduction

Landfill gas, a mixture of methane and carbon dioxide generated by the anaerobic decomposition of municipal solid waste, is a natural resource in many ways similar to low quality natural gas. Methane generation at U.S. landfills is estimated to equal about 5% of domestic natural gas consumption, or 1% of domestic total energy needs. The amount of landfill gas produced by a municipal landfill is significant; 3 to 5 million standard cubic feet per day (SCF/day) is typical for landfills found in or near all large metropolitan areas. Both methane and carbon dioxide are potential products from this largely wasted gas resource. An excellent overview article entitled "Landfills are #1" was presented a few years back in *Garbage* [1], also see Rathje [2].

A major barrier to widespread utilization of landfill gas (LFG) for energy and merchant carbon dioxide is reliable, economic removal of contaminants from the raw gas. Landfill gas contaminants challenge separation technology several ways: 1) *potential* contaminants include literally hundreds of chemical compounds, among them toxic species such as vinyl chloride and hydrogen sulfide, 2) each landfill has a unique contaminant lineup, and 3) the contaminant lineup changes throughout the landfill's gas production life.

Acrion has developed technology to remove contaminants from LFG with in-situ *cold liquid* carbon dioxide obtained directly from LFG. (The technique uses conditions distant from the widely publicized component extraction with *supercritical* carbon dioxide.) A stream of contaminant-free methane and carbon dioxide is produced as feedstock for methanol synthesis; with further processing to separate carbon dioxide, pipeline methane and liquid carbon dioxide are produced. The contaminant laden carbon dioxide stream is incinerated in the landfill flare.

Acrion's liquid CO₂ wash technology is unique in several ways: 1) the contaminant separating agent, liquid CO₂, is obtained directly from raw LFG, eliminating the need to purchase, store and dispose of separating agents such as organic solvents and solid sorbents; 2) cold liquid CO₂, a physical solvent insensitive to type of contaminant, requires no process modification as LFG contaminant composition changes with time; 3) energy invested in LFG compression is preserved during bulk CO₂ removal, permitting economic recovery of high pressure liquid CO₂; 4) LFG contaminants are concentrated for efficient incineration, reducing NO_x and other air emissions; and 5) CO₂ wash, based on conventional chemical engineering

unit operations, affords low technical risk for production of a variety of fuels and chemicals derived from methane and CO₂, depending on local market needs.

Objectives

The principal research objective is development of a process to recover contaminant-free reformer feedstock for methanol synthesis from raw landfill gas. Unlike currently available gas-cleaning technologies, *one processing step* can efficiently and simultaneously adjust the methane/carbon dioxide ratio for methanol synthesis and remove the broad and variable spectrum of trace contaminants present in raw LFG. Measurements taken in Phase I from a pilot scale absorber confirm the inherent ability of liquid carbon dioxide to remove all contaminants except for hydrogen sulfide. Hydrogen sulfide is reduced to levels sufficient for removal by standard guard beds which are an integral part of a methanol synthesis train. Construction of a LFG to methanol facility based on this process will provide:

- Immediate environmental and safety benefits at and adjacent to landfill sites,
- Secondary environmental benefits derived from vehicles using clean burning methanol or oxygenated gasoline (the MTBE in reformulated gasoline is made from methanol),
- Methanol fuels produced from landfill gas can reduce net greenhouse gases; the organic fraction of municipal solid waste consumes carbon dioxide during its formation which is released during methanol combustion, a “mini carbon cycle,”
- Reliable local supplies of methanol fuel not subject to long distance transport costs, and which decrease dependence on foreign energy sources,
- Urban methanol produced from landfill gas can augment farm-belt ethanol derived from corn to help increase the supply of oxygenates for reformulated gasoline derived from renewable/recycled sources,
- Increased supplies of low cost methanol in major metropolitan areas for non-fuel uses, such as resin manufacture, which can increase job opportunities.

Technical Approach

Acirion’s technology converts LFG to a high pressure mixture of contaminant-free methane and carbon dioxide for methanol synthesis feedstock. The LFG recovery process, for the most part conventional compression, cooling and condensation, relies on the excellent solvent properties of cold liquid carbon dioxide to remove contaminants. The absorber temperature and pressure are selected to provide a product gas containing methane and carbon dioxide in the desired ratio for reforming to methanol synthesis gas, about 2.3 CH₄ per CO₂. The contaminant-free methane-carbon dioxide recovered from LFG in the mole ratio about 2.3:1 is mixed with steam and reformed to carbon monoxide and hydrogen. Methanol synthesis is by conventional low pressure (about 1,000 psia) technology. Figure 1 is a simple schematic of the entire process, from raw LFG to methanol.

Liquid carbon dioxide, as opposed to organic solvents, is inert with respect to trace contaminants, and possesses other properties desirable of an absorbent physical solvent as shown in Table 1.

Figure 1
Landfill Gas to Methanol Process Schematic

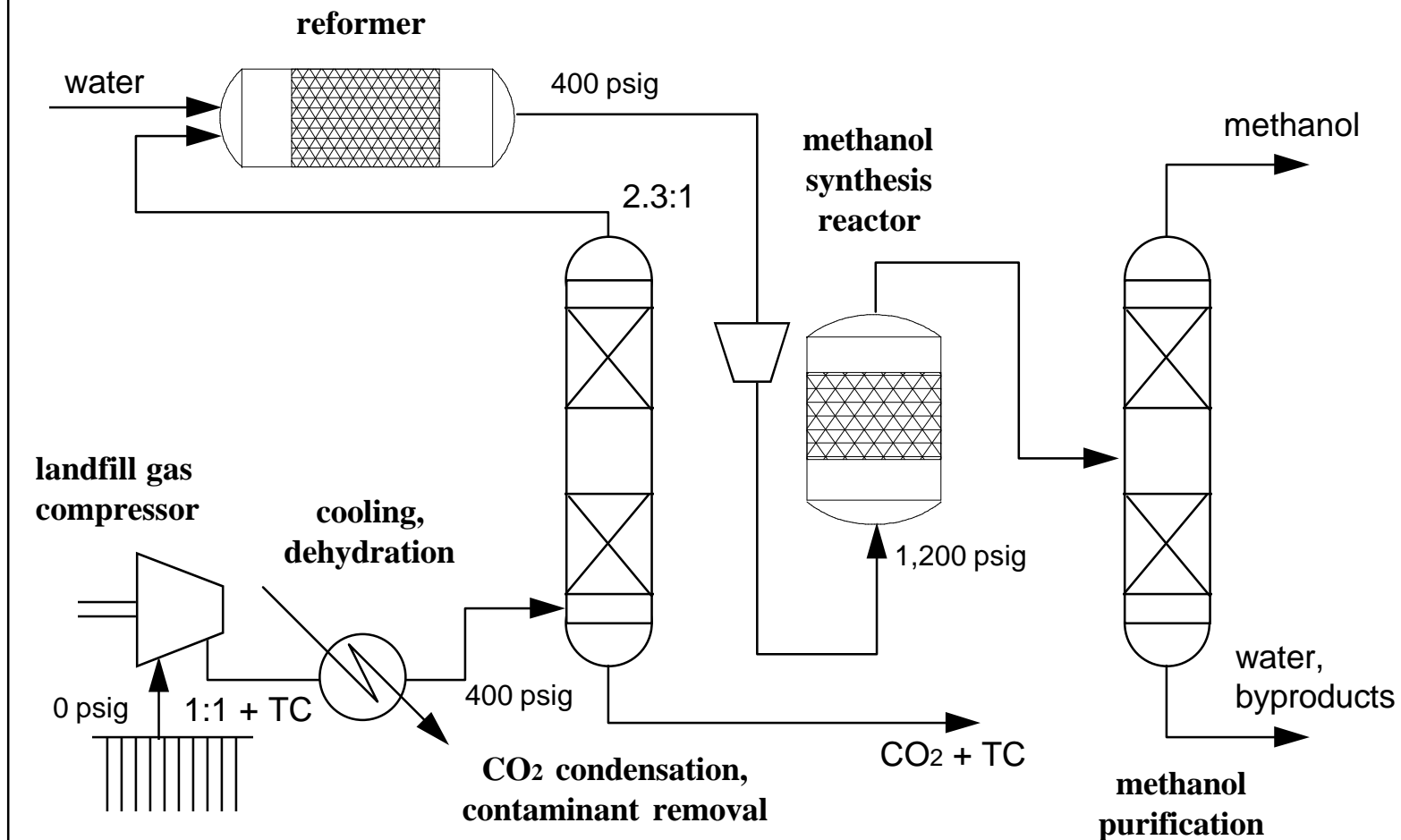


TABLE 1
FEATURES OF COLD LIQUID CARBON DIOXIDE SOLVENT

- Attractive physical properties
 - low viscosity, ≈ 0.2 centipoise (-45°C)
 - high density, $\approx 71 \text{ lb/ft}^3$ (-45°C)
 - low molecular weight, 44
 - low surface tension
- Favorable equilibrium for trace contaminants [3,4]
- High absorber stage efficiency [4]
- Continuously available from raw landfill gas, no regeneration required
- Non-combustible, non-toxic, environmentally benign “green” solvent

These characteristics make liquid CO_2 the preferred solvent for the most critical step of a LFG to methanol process -- economic removal of LFG contaminants from methane and CO_2 to very low levels. (The technology uses liquid carbon dioxide as a conventional absorbent generally at temperatures below 0°C , not to be confused with supercritical CO_2 extraction technology.) Amines and other organic solvents often react irreversibly with contaminants to form species which foam, become viscous, or otherwise hinder the desired separation. Even chemically inert organic solvents, once contaminated, are difficult to regenerate; Rousseau [5] has shown that methanol, among other solvents, is not easily regenerated with respect to organic trace contaminants by pressure reduction or heating.

Table 2 summarizes various levels of LFG abatement, treatment, and recovery. Control of contaminants and recovery of valuable by-products become more complete proceeding from Case 0) to 5). Case 4), LFG compression and CO_2 removal by condensation, is the technical basis of the proposed LFG to methanol process. Acrion's contaminant removal makes Case 5), carbon dioxide removal from a contaminant-free landfill gas, a relatively simple task which can be accomplished with a number of commercial processes.

Project Description

A concise one-page summary of the Phase I program is shown in Table 3.

Results/Accomplishments

The ability of liquid carbon dioxide to absorb LFG contaminants was confirmed in Phase I. A pilot scale absorption column, constructed and operated in Acirion's laboratory, was used to measure the absorption of six contaminants: dichlorodifluoro-methane (Freon-12), methyl chloride, acetone, pentane, ethanol and ethylene dichloride. Gas phase contaminant concentrations were reduced by factors ranging from 100 to 5000, often to levels

TABLE 2
LEVELS OF LANDFILL GAS TREATMENT

Case 0) Landfill Gas Not Collected, Escapes to Atmosphere
<ul style="list-style-type: none"> • carbon dioxide and methane are greenhouse gases • methane migration and odors uncontrolled
Case 1) Landfill Gases Collected and Flared
<ul style="list-style-type: none"> • methane converted to less potent greenhouse gas CO₂ • methane migration and odors mitigated
Case 2) Dehydration
<ul style="list-style-type: none"> • low Btu fuel gas • electricity generation
Case 3) Dehydration, Compression, Contaminant Removal
<ul style="list-style-type: none"> • clean LFG for electricity generation • clean low Btu fuel gas
Case 4) Dehydration, Compression, Contaminant Removal with Liquid CO₂
<ul style="list-style-type: none"> • clean LFG for electricity generation • clean medium Btu fuel gas • clean LFG as feedstock for methanol synthesis
Case 5) Carbon Dioxide Removal
<ul style="list-style-type: none"> • clean high Btu fuel or pipeline gas • conversion to liquid methane

below the detection limit of Acrion's analytical equipment. These results show that Freon-12 and methyl chloride, among the more difficult contaminants to remove from LFG, can be reduced to levels which will not poison methanol synthesis catalysts.

Economic estimates for the proposed LFG process, based in part on GRI developed guidelines [6], have been prepared for a prototype LFG to methanol plant. The economic summary is presented in Tables 4 and 5, together with two other alternative scenarios for products from landfill gas: 1) pipeline gas + liquid CO₂, and 2) liquid methane + liquid CO₂. The plants are based on 4.0 million SCF/day of raw landfill gas feed.

The estimated capital requirement for the methanol case is \$11.4 million (1996\$), of which nearly 80% or \$9.0 million is Acrion's capital estimate for gas reforming, methanol synthesis and methanol purification. Methanol revenues do not include the section 40 tax credit of 54¢/gal for alcohol fuel from a renewable source. Also, section 29 tax credits of approximately \$1 per MMBtu for landfill gas use are not considered.

TABLE 3
PHASE I PROGRAM SUMMARY
CONTRACT DE-FG02-91ER81690
LANDFILL GAS CONVERSION TO A CONTAMINANT-FREE METHANE-CO₂ REFORMER
FEEDSTOCK FOR METHANOL SYNTHESIS

Task	Objective	Status	Result
Task 0 Review Work Plan	Pre contract review	Complete ✓	Industry interaction resulted in addition of Task 1A. Existing equipment tested.
Task 1 Reconfigure Experimental Components	Assemble equipment for Task 2	Complete ✓	Steel skid and support frame built. Procurement of supplies. Existing equipment assembled into functioning system on new skid.
Task 1A (additional) Design & Build New Absorber	Design, build & test vessel made from killed carbon steel	Complete ✓	Vessel constructed, performed well in testing. Will result in significantly lower capital cost for commercial venture.
Task 2 Operate Absorber	Acquire data demonstrating contaminant removal with liquid CO ₂ absorbent	Complete ✓	Eight contaminants studied; expanded process data base; proven ability to absorb contaminants with liquid CO ₂ .
Task 3 Analyze Experimental Data	Compare experimental data to computer simulations; analyze absorber effectiveness	Complete ✓	Data compared well with process simulation; results increase confidence of potential commercialization partners.
Task 4 Process Design & Economics	Establish technical and economic feasibility	Complete ✓	Process simulated; technical and economic viability established.
Task 5 Commercial Contacts	Seek industrial support and commercial opportunities	Complete ✓	Positive response from industry; commercialization probable following technical demonstration at landfill with raw LFG.
Task 6 Final Report	Summarize and communicate successful Phase I results	Complete ✓	Phase I data and process design summary; technology transfer tool for Phase III commercialization effort.

TABLE 4
PRODUCT SCENARIOS FROM 4 MILLION SCF/DAY LANDFILL GAS
(54% methane, 46% carbon dioxide)

<i>Product</i>	<i>Units/Day</i>	<i>Selling Price</i>	<i>Sales/yr \$million</i>	<i>Capital \$million</i>	<i>Operating \$million/yr</i>	<i>Net Revenue \$million/yr</i>
pipeline gas	2,249 MMBtu	\$2/MMBtu	1.4	7.7	0.96	1.56
liquid CO ₂	88 ton	\$40/ton	1.2			
liquid methane	19,000 gallon	35¢/gal	2.3	9.6	0.76	2.44
liquid CO ₂	66 ton	\$40/ton	0.9			
methanol	22,000 gallon	48¢/gal	3.70	11.4	0.86	2.84

TABLE 5
INVESTMENT BENCHMARKS

Product	Pipeline Gas Liquid CO ₂	Liquid Methane Liquid CO ₂	Methanol
Investment, \$million	7.7	9.6	11.4
Simple Payback, yrs	4.7	3.9	4.0
Payback @ 12%, yrs	7.3	5.7	5.8
NPV @ 12%, \$million	4.6	8.6	9.8
IRR	19.2%	24.4%	23.9%

Table 6 briefly compares the relative advantages and disadvantages of several technologies for LFG upgrade. Selexol and cold methanol are representative of physical solvents, while Prism is a representative membrane technology. Solid bed adsorbents are represented by activated carbon, zinc or iron oxide, and zeolites, to name a few. Each has been developed to remove a class of contaminant, e.g., oxides to remove H₂S, activated carbon for chlorinated compounds and aromatic hydrocarbons, and zeolites to remove other sulfur compounds and light hydrocarbons. The raw LFG must be well characterized to implement solid sorbent beds without excessive overkill. Also, as the contaminant species change over the landfill's life, sorbent beds may need to be changed, or additional beds added. Zinc oxide is not regenerable, while activated carbon and zeolites lose adsorptive capacity with each regeneration due to poisoning. The spent bed in many cases is classified hazardous waste due to the accumulated trace contaminants.

Applications/Benefits/Features

The proposed LFG to methanol process offers a number of features, advantages and benefits compared to prior process configurations proposed for LFG to methanol, e.g., Ham [7].

<p style="text-align: center;">TABLE 6</p> <p style="text-align: center;">COMPARISON OF LANDFILL GAS TREATMENT PROCESSES</p>		
Process	Advantages	Disadvantages
Contaminant and CO ₂ removal with physical solvents (<i>Selexol</i>) (<i>Cold Methanol</i>)	commercial process complete methane recovery possible	CO ₂ not recovered (CO ₂ recovery requires compression a second time) potential build-up of trace contaminants in solvent make-up solvent required
Contaminant and CO ₂ removal with membranes (<i>Prism</i>)	commercial process simplistic design and operation	significant unrecovered methane CO ₂ not recovered (CO ₂ recovery requires compression a second time) potential presence of trace contaminants in methane potential membrane degradation by trace contaminants
Contaminant removal with solid adsorbents	commercial process for non LFG industries simple, low pressure operation	carbon dioxide must be removed by other technology multiple adsorbents required to remove multiple contaminants finite bed life and disposal problems
Contaminant and CO ₂ removal by condensation and liquid CO ₂ absorption (<i>Acrion</i>)	contaminant-free methane and CO ₂ recovery as feedstocks or commodity chemicals complete methane recovery possible absorbent CO ₂ obtained from raw LFG; no additional chemicals requiring make-up or disposal contaminants concentrated for easier disposal by incineration	no commercial operation to date liquid CO ₂ absorption of chlorine, sulfur, and hydrocarbon compounds demonstrated at scale of 10,000 SCFD gas flow

Trace Contaminant Removal: Trace contaminants are effectively scrubbed from the raw LFG by liquid CO₂ absorbent, a fluid continuously condensed directly from LFG. No make-up chemicals or solvents are needed; disposal of spent solvent is not a concern. Spent liquid CO₂ solvent is not regenerated, but sent with contaminants to incineration. Based on experimental data compiled by Acrion in Phase I and examination of typical contaminant vapor pressures, liquid carbon dioxide is the solvent of choice for continued removal of the changing and often unidentified slate of trace contaminants from LFG over the gas production life of a landfill.

Utilization of LFG CO₂ as Carbon Source for Synthesis Gas: Methane is hydrogen-rich, carbon-poor as a feedstock for methanol synthesis. Reforming methane with steam yields H₂:CO = 3:1; the ratio desired for methanol synthesis is 2:1. Thermodynamic equilibrium calculations, and discussions with methanol plant vendors, indicate the ratio of methane to CO₂ in the reformer feedstock should be about

2.3:1 to obtain the highest equilibrium conversion to methanol. Careful selection of the temperature and pressure of contaminant absorption and CO₂ condensation yields a contaminant-free mixture of methane and CO₂ with the desired 2.3:1 ratio. Conversion of LFG CO₂ as well as methane to methanol reduces greenhouse gas emissions of methane and CO₂.

Dual Utilization of LFG Pressurization: Capital and energy invested to compress raw LFG for contaminant absorption and CO₂ condensation is not dissipated by pressure letdowns in the separation sequence. Both the methane-CO₂ product gas and the liquid CO₂ containing the contaminants is available at the contaminant absorber operating pressure, about 400 psia. Since the contaminated CO₂ is available at high pressure as a liquid, it may be adiabatically expanded to provide cooling. Most of the process refrigeration requirements can be met in this manner. The flashing of high pressure solvents laden with CO₂ is thermodynamically irreversible and does not provide opportunity for energy recovery. Product gas mixed with steam passes to the reformer operating at about 400 psia, and the reformer outlet is then boosted to methanol synthesis pressure of about 1,200 psia.

Process Energy Requirements Met by LFG: Process thermal energy requirements, primarily reformer heat, are met by combusting a portion of the raw LFG feed. Approximately 30% of the 3.8 million SCF/day raw LFG is consumed for this purpose. Synthesis reactor waste heat boilers raise steam used to generate process electric power requirements.

Contaminants Isolated in Small Stream for Effective Destruction by Incineration:

Carbon dioxide condensate, a high pressure liquid, contains the LFG trace contaminants. Eventual incineration of trace contaminants requires less fuel and generates less NO_x because the contaminants are concentrated in a relatively small stream requiring less fuel gas and air for combustion.

Methanol More Easily Produced, Stored, and Distributed than LNG: Methanol production from LFG requires that trace contaminants be removed to low levels, but not CO₂; the feedgas for methanol synthesis preferably contains 30% CO₂. This contrasts with LNG production from LFG wherein not only trace contaminants must be removed to low levels, but CO₂ also must be removed to 50 ppm or less to prevent solidification during methane liquefaction. Process energy requirements for methanol synthesis are largely thermal (static heat exchangers) rather than mechanical (recip or rotating compressors) as in the refrigeration-based LNG production. Finally, methanol is stored and transported in conventional tanks, rail cars, and barges as a liquid at normal ambient pressure and temperature (b.p. 64.5°C), whereas storage and transport of LNG require well-insulated cryogenic vessels rated for modest internal pressures (b.p. -161.7°C).

Phase I Conclusions

The operation of an absorption column demonstrating the effectiveness of in-situ liquid carbon dioxide absorbent in removing trace contaminants was a success. Phase I efforts confirm the technical and economic viability of Acirion's proposed LFG to methanol process. A process simulation based on experimental results clearly shows commercialization potential. Process economics are attractive; the simple payback period on capital is estimated to be 4.0 years (without tax credits) for a plant processing 4.0 million SCF/day of raw LFG and producing 22,000 gal/day methanol. The market for methanol exists and is growing. Industry finds Acirion's LFG recovery technology to be superior and versatile. Continued aggressive

experimental demonstration and process development through Phase II will convince third parties to finance the first commercial embodiment of Acrion's LFG to methanol technology during Phase III.

Future Activities

Phase II objective is to demonstrate production of contaminant-free methanol synthesis feedstock gas from raw landfill gas by contaminant absorption with cold liquid carbon dioxide. The amount of raw LFG gas will be about 100,000 SCF/day, a scale sufficient to demonstrate both technical and commercial viability to municipal landfill owners/operators and project developers. Several host landfill sites in Ohio, Pennsylvania and New Jersey are being considered.

Contract Information

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